

## LOW SEDIMENT FRICTION MODIFIERS

### BACKGROUND OF THE INVENTION

#### 1. Technical Field

The present invention relates to friction modifiers for lubricant oils used, for example, in engines for motorized vehicles.

#### 2. Description of the Related Art

Friction modifiers for enhancing the lubricity of lubricant oils are known. Typical friction modifiers include esters of glycerol and fatty acids, overbased carboxylates, and oxidized petroleum fractions. Also known is the use of detergent additives such as overbased calcium sulfonates. However, a common problem which occurs when aging the lubricant oil is the formation of sediment.

During storage, especially under warm temperature conditions, sedimentation occurs in stocks of lubricant oils containing friction modifiers and detergent additive. In a storage tank containing many thousands of gallons of lubricant oil fluid, a sedimentation rate of a few percent can correspond to a thousand or more gallons of bottom sediment, which is clearly undesirable. What is needed is an additive for lubricant oils which provides a friction modifier and detergent, and which is characterized by a low sedimentation rate.

### SUMMARY

An additive mixture for lubricant oils is provided herein. The additive mixture comprises: (a) an overbased alkaline earth metal sulfonate; and, (b) at least one friction modifier selected from the group consisting of an overbased alkaline earth carboxylate, the reaction

product of an alkanolamine with a fatty acid or a fatty acid ester, the reaction product of thiodiglycol with a fatty acid or a fatty ester and the reaction product of a dialkylene glycol with a fatty acid or a fatty ester.

The additive mixture provides a lubricant oil composition having improved lubricity and exhibits less sedimentation.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Various embodiments are described below with reference to the drawings wherein:

FIG. 1 is a graph illustrating the sedimentation results of Example 75; and,

FIG. 2 is a graph illustrating the friction test results of Example 76.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENT(S)

Lubricating oil compositions used to lubricate the moving parts of engines, especially internal combustion engines, contain base oil of lubricating viscosity, or a mixture of such oils, and additives used to improve the performance characteristics of the oil. For example, additives are used to improve detergency, reduce engine wear, to provide stability against heat and oxidation, to reduce oil consumption, to inhibit corrosion, to act as a dispersant, and reduce friction loss. Some additives provide multiple benefits, such as a dispersant/viscosity modifier. Other additives, while improving one characteristic of the lubricating oil, have an adverse affect on other characteristics. Thus to provide a lubricating oil having optimal overall performance, it is necessary to characterize and understand all the effects of the various additives available, and carefully balance the additive content of the lubricant.

The present invention is a low sediment additive mixture for lubricant oils which comprises an overbased alkaline earth metal sulfonate with a selected friction modifier.

The additive mixture can be added to any type of lubricant oil including metal cutting and drawing oils, although motor oils are preferred. The lubricant oils can be natural or synthetic. Natural oils include petroleum oils, solvent-treated, acid treated or hydrotreated mineral oils, coal oil and shale oil. The lubricant oil can include saturated, olefinic unsaturated and aromatic components. Furthermore, the lubricant oil can include hydrocarbon and/or non-hydrocarbon components such as fatty acids and fatty acid esters.

Overbased alkaline earth sulfonates are detergent compounds prepared by neutralizing a sulfonic acid with an excess of alkaline earth metal base (e.g., the hydroxides of magnesium, calcium or barium) so as to produce an overbased alkaline earth metal sulfonate with a total base number ("TBN") of greater than zero. The TBN is the amount of acid needed to neutralize all of the alkalinity of the overbased material, and can be determined according to ASTM D 2896. A composition with a TBN of about 100 or less is considered to be a "low overbased material." A TBN of about 100 to 300 is characterized as "moderate overbasing." A composition with a TBN of over 300 is considered to be a "highly overbased" material. The preferred overbased alkaline earth metal sulfonate is overbased calcium sulfonate having a TBN of above about 250, preferably above about 350, and more preferably 400 or higher.

In one aspect of the invention it has been found that amorphous overbased calcium sulfonate is superior to crystalline calcium overbased sulfonate in terms of undesired sedimentation. An amorphous overbased calcium sulfonate suitable for use in the present invention is commercially available from Crompton Corporation of Middlebury CT under the designation Calcinat<sup>TM</sup> C-400 CLR. The amorphous overbased calcium sulfonate has a particle size of less than about 30 nm. Crystalline overbased calcium sulfonates have a particle size above 30 nm, preferably 50-500 nm and more preferably 50-100 nm. Calcinat<sup>TM</sup> C-300CS, available from Crompton Corporation, is an example of a crystalline overbased calcium

sulfonate. A method for preparing highly overbased calcium sulfonate is described in U.S. Patent No. 6,444,625 B1, which is herein incorporated by reference.

In another aspect of the invention it has been found that certain friction modifiers, when combined with an overbased alkaline earth sulfonate, exhibit lower sedimentation properties.

The lubricant composition also comprises a friction modifier to reduce the coefficient of friction. The friction modifier and overbased calcium sulfonate can be combined and packaged with other additives such as antioxidants, dispersants and/or defoamers, or other types of additives such as mentioned above.

Various friction modifiers can be used in the additive mixture. Such friction modifiers include glycerol monoesters, overbased carboxylates, overbased tall oil fatty acids, the reaction product of an alkanolamine (e.g., triethanolamine ("TEA") or diethanolamine) or a glycol (e.g., thiodiglycol, diethylene glycol) with a fatty acid or fatty ester, oxygenated petroleum fractions, alkoxylated alkylamine and the reaction products of glycols with fatty esters.

Glycerol monoesters useful as friction modifiers include, for example, glycerol esters of saturated or unsaturated C<sub>8</sub> to C<sub>20</sub> fatty acids such as glycerol monopalmitate, glycerol monostearate, glycerol monooleate, and the like.

Overbased carboxylates are known and are generally prepared by reacting an acidic material, normally an acidic gas such as SO<sub>2</sub> or CO<sub>2</sub>, and most commonly carbon dioxide, with a mixture comprising a carboxylic acid and a stoichiometric excess of an alkaline base metal compound in a reaction medium, preferably with a promoter. The base metal is preferably an alkaline earth metal such as magnesium, calcium or barium in the form of an oxide or hydroxide. The carboxylic acid is preferably a saturated or unsaturated carboxylic acid having from about 8 to about 30 carbon atoms. Useful carboxylic acids include, but are not limited to, caprylic acid, capric acid, lauric acid, myristic acid, myristoleic acid, decanoic acid, dodecanoic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, margaric acid, stearic acid, 12-

hydroxystearic acid, oleic acid, ricinoleic acid, linoleic acid, arachidic acid, gadoleic acid, eicosadienoic acid, behenic acid, erucic acid, mixtures of any of these acids or their reactive equivalent.

Other suitable overbased carboxylates include overbased calcium tallate and overbased barium tallate.

A reaction product of TEA and fatty ester suitable for use as a friction modifier is the reaction product of TEA and methyl oleate. Other suitable friction modifiers include the reaction products of TEA with, for example, oleic acid, ricinoleic acid, isostearic acid, erucic acid, tall oil fatty acid (TOFA), mixed oleic/stearic acids, and iso-oleic acid.

Oxygenated petroleum fractions are known. Petroleum oxidates and methods for making them are disclosed in U.S. Patent No. 5,439,602, which is herein incorporated by reference.

Also suitable for use as friction modifiers are the reaction products of thiodiglycol with fatty acids or fatty esters (e.g., oleic acid, methyl oleate, etc.), and the reaction products of a dialkylene glycol (e.g., diethylene glycol, dipropylene glycol, etc.) with a fatty acid or fatty ester (e.g., oleic acid, methyl oleate, etc.).

In another aspect of the invention it has been found that overbased alkaline earth sulfonate (especially crystalline overbased calcium sulfonate) provides a lubricant oil composition with greater lubricity (i.e., lower coefficient of friction). Particularly preferred as a friction modifier are the reaction products of TEA with fatty acids or fatty esters for both excellent lubricity and low sedimentation. A preferred crystalline overbased calcium sulfonate is available from Crompton Corp. under the designation Calcinate C300CS and has a particle size of about 50-500 nm. Preferred particle size for a crystalline overbased calcium sulfonate ranges from about 50 nm to about 100 nm.

The following Examples illustrate features of the invention. In one type of experiment, illustrated below in Examples 1-30 and 59-75, lubricant oils containing a selected overbased

calcium sulfonate and a selected friction modifier were tested for sedimentation. In another type of experiment, exemplified in Examples 31-58 and 76, the lubricant oils containing combinations of selected overbased calcium sulfonates and friction modifiers were tested for friction reducing characteristics.

### Examples 1-8

These examples are directed to a study of the sedimentation characteristics of various blends of overbased calcium sulfonate and selected friction modifiers. Two types of overbased calcium sulfonates were individually tested. Calcinat<sup>TM</sup> C300CS is a crystalline overbased calcium sulfonate having TBN of about 300 and a particle size of from about 50nm to about 100 nm, and is available from Crompton Corporation. Calcinat<sup>TM</sup> C400CLR is an amorphous overbased calcium sulfonate available from Crompton Corporation having TBN of about 400 and a particle size of no more than about 30 nm. Overbased calcium sulfonates were present in 10% concentrations. The friction modifier included glycerol mono oleate ("GMO").

Polyisobutylene succinic anhydride ("PIBSA") having a molecular weight of about 1,050, was present in Examples 3, 4, and 7 as a dispersant. The friction modifier was present in 1% concentrations when employed. The lubricant oil stock was a severely hydrotreated naphthenic oil available from Ergon, Inc. under the designation Hyprene H100. Hyprene H100 is characterized by an API gravity (60°F) of 24.6, a pour point of -50°F, and an aniline point of 163°F. The respective overbased calcium sulfonate and friction modifier were combined with the diluent lubricant stock and placed in a 100 ml centrifuge tube in a 70°C oven for a period of 12 weeks. The sediment formed was measured at one week intervals and recorded as percentages. In examples 1 and 5, no friction modifiers were employed. It can be seen that use of the amorphous overbased calcium sulfonate Calcinat C400CLR (Examples 5-8) reduces sedimentation dramatically. It is believed that the reduced sedimentation of the amorphous variety of overbased calcium sulfonate is related to its smaller particle size.

The results of these experiments are set forth in Table 1.

The sediments formed in the Calcinat<sup>TM</sup> C300CS Examples 1 to 4 were analyzed by FTIR by removing an aliquot of sediment from the bottom layer with a pipette. In all sediments

there was a strong peak at  $881\text{ cm}^{-1}$ , which is an indication of  $\text{CaCO}_3$  in the calcite form. There were no peaks observed from sulfonate, which did not precipitate with the calcite.



TABLE 1

Example	1	2	3	4	5	6	7	8
C300CS	10%	10%	10%	10%	---	---	---	---
C400CLR	---	---	---	---	10%	10%	10%	10%
PIBSA	---		1%	1%	---	---	1%	1%
GMO	---	1%	---	1%	---	1%	---	1%
Hyprene H100	90%	89%	89%	88%	90%	89%	89%	88%
% Sediment, 70°C @ Week								
1	0.01	0.35	0.55	0.35	0	0	0	0
2	0.35	0.25	0.50	0.30	0	0	0	0
3	0.30	0.30	0.50	0.30	0	0	0	0
4	0.30	0.30	0.65	0.25	0	0	0	0
5	0.25	0.25	0.50	0.30	0	0	0	0
6	0.25	0.25	0.30	0.25	0.001	0.002	0.001	0.002
7	0.30	0.25	0.40	0.25	0.002	0.002	0.001	0.002
8	0.25	0.25	0.40	0.25	0.002	0.002	0.001	0.005
9	0.25	0.25	0.35	0.25	0.002	0.002	0.002	0.005
10	0.25	0.25	0.40	0.25	0.002	0.002	0.002	0.005
11	0.25	0.25	0.35	0.25	0.002	0.002	0.005	0.010
12	0.25	0.25	0.35	0.25	0.002	0.002	0.005	0.010
Final centrifuge	0.25	0.20	0.35	0.25	0.001	0.002	0.002	0.005

### Examples 9 to 16

Sedimentation experiments were conducted in the same manner as in Examples 1-8 except that the friction modifiers tested were an oxidized petroleum fraction available under the designation Alox 165L from Lubrizol, an overbased calcium oleate, designated herein as “OCO”, and GMO. The friction modifiers, when employed, were each present in 0.5% concentration. Examples 10 and 14 did not employ any friction modifiers.

As can be seen from the results the amorphous overbased calcium sulfonate Calcinat<sup>TM</sup> C400CLR (Examples 13-16) was characterized by very low sedimentation percentages (typically about 0.001 to about 0.005) as opposed to the sedimentation percentages (0.11 to 0.50) for the Calcinat<sup>TM</sup> C300CS (Examples 9-12).

The results of these experiments are set forth in Table 2.

TABLE 2

Example	9	10	11	12	13	14	15	16
C300CS	10%	10%	10%	10%	---	---	---	---
C400CLR	---	---	---	---	10%	10%	10%	10%
Alox 1652	0.5%	---	---	---	0.5%	---	---	---
OCO	---	---	0.5%	---	---	---	0.5%	---
GMO	---	---	---	0.5%	---	---	---	0.5%
Hyprene H100	89.5%	90	89.5	89.5	89.5	90	89.5	89.5
% Sediment, 70°C @ Week								
1	0.50	0.40	0.02	0.40	0.001	0.001	0.001	0.001
2	0.40	0.35	0.03	0.30	0.001	0.001	0.001	0.001
3	0.35	0.30	0.02	0.30	0.001	0.001	0.001	0.001
4	0.35	0.30	0.05	0.30	0.001	0.001	0.001	0.001
5	0.35	0.30	0.11	0.30	0.001	0.001	0.001	0.001
6	0.30	0.25	0.20	0.25	0.001	0.001	0.001	0.002
7	0.30	0.25	0.40	0.25	0.005	0.002	0.002	0.002
8	0.30	0.25	0.20	0.25	0.005	0.005	0.002	0.005
9	0.30	0.25	0.20	0.25	0.005	0.005	0.002	0.005
10	0.30	0.25	0.20	0.25	0.005	0.005	0.002	0.005
11	0.30	0.25	0.25	0.25	0.005	0.005	0.005	0.005
12	0.30	0.25	0.25	0.25	0.005	0.005	0.005	0.005
Final centrifuge	0.30	0.25	0.20	0.25	0.005	0.002	0.002	0.002

### Examples 17 to 28

Sedimentation experiments were conducted in a manner similar to Examples 9 to 16, except that the friction modifiers tested were OCO (overbased calcium oleate), Alox 302 (oxygenated petroleum fraction), an overbased barium tallate having 3% -10% barium and designated herein as "OBT", an overbased calcium tallate having 4%-10% calcium and designated herein as "OCT", and GMO (glycerol mono oleate). Examples 22 and 28 did not employ any friction modifier.

As can be seen, the amorphous overbased calcium sulfonate Calcinat<sup>TM</sup> C400CLR (Example 23-28) is characterized by much lower percentages of sedimentation as opposed to the sedimentation percentages for the crystalline overbased calcium sulfonate Calcinat<sup>TM</sup> C300CS (Examples 17-22).

The results of these experiments are set forth in Table 3

TABLE 3

Example	17	18	19	20	21	22	23	24	25	26	27	28
C300CS	10%	10%	10%	10%	10%	10%	---	---	---	---	---	---
C400CLR	---	---	---	---	---	---	10%	10%	10%	10%	10%	10%
OCO	0.5%	---	---	---	---	---	0.5%	---	---	---	---	---
Alox 302	---	0.5%	---	---	---	---	---	0.5%	---	---	---	---
OBT	---	---	0.5%	---	---	---	---	---	0.5%	---	---	---
OCT	---	---	---	0.5%	---	---	---	---	---	0.5%	---	---
GMO	---	---	---	---	0.5%	---	---	---	---	---	0.5%	---
Hyprene	89.5%	89.5	89.5	89.5	89.5	90	89.5	89.5	89.5	89.5	89.5	90
% Sediment 70°C @ Week												
1	0.001	0.001	0	0	0.45	0.01	0	0	0	0	0	0
2	0.002	0.35	0.01	0.01	0.35	0.25	0	0	0	0	0	0
3	0.030	0.40	0.02	0.04	0.35	0.25	0	0	0.001	0.001	0.001	0.001
4	0.030	0.35	0.05	0.05	0.30	0.25	0	0.001	0.001	0.001	0.001	0.001
5	0.030	0.30	0.03	0.075	0.25	0.25	0.001	0.001	0.002	0.002	0.001	0.001
6	0.030	0.40	0.04	0.10	0.25	0.25	0.001	0.001	0.001	0.001	0.001	0.001
7	0.040	0.35	0.04	0.10	0.25	0.30	0.001	0.001	0.002	0.002	0.001	0.001
8	0.040	0.35	0.05	0.15	0.25	0.30	0.001	0.002	0.002	0.002	0.001	0.002
9	0.050	0.30	0.05	0.15	0.25	0.20	0.001	0.002	0.002	0.002	0.001	0.002
10	0.050	0.30	0.05	0.15	0.25	0.25	0.001	0.002	0.002	0.002	0.001	0.002
11	0.070	0.30	0.05	0.15	0.25	0.25	0.001	0.002	0.002	0.002	0.002	0.002
12	0.070	0.30	0.05	0.15	0.25	0.25	0.001	0.001	0.002	0.002	0.002	0.002

### Examples 29 to 30

Sedimentation experiments were conducted in the same manner as in the previous examples except that the friction modifiers included 0.5% of a reaction product of TEA and tall oil fatty acid resulting in a trioleate ester, which is designated herein as "TEA-T".

The results set forth in Table 4 illustrate that the amorphous overbased calcium sulfonate Calcinat<sup>TM</sup> C400CLR was (Examples 31, 32) was characterized by much lower sedimentation percentages than the sedimentation percentages for crystalline overbased calcium sulfonate Calcinat<sup>TM</sup> C300CS. But also the use of TEA-T as a friction modifier with Calcinat<sup>TM</sup> C300CS surprisingly provided a lubricant blend with much lower sedimentation than that employing the GMO/ET-2 friction modifier.

**TABLE 4**

Example	29	30
C300 CS	10%	---
C400 CLR	---	10%
TEA-T	0.5%	0.5%
GMO	---	---
Hyprene H100	89.5%	89.5%
Total % Sediment @ 70°C Week:		
1	0.001	0
2	0.010	0.001
3	0.020	0.001
4	0.020	0.001
5	0.020	0.002
6	0.030	0.001
7	0.040	0.002
8	0.050	0.002
9	0.050	0.002
10	0.050	0.002

### Examples 31-44

These Examples are directed to the friction reducing characteristics of the lubricant oil blends. The coefficient of friction for the selected blends was measured with a Cameron-Plint

TE-77 high frequency friction test. The conditions are set forth below

Upper specimen 6mm X 16mm Dowel EN 1A (BS 1804 Part 1 Grade 1, 220M07)  
Lower specimen Flat hardened ground NSOH BO1 Gauge Plate (RC 60/0.4  $\mu$ m)  
Frequency 5 Hz  
Load (N) 50-100  
Amplitude 15 mm

#### **Temperature Profile for Cameron Plint Test**

Stage	Load (N)	Ramp Time (min)	Temperature °C	Dwell Time (min)
1	0	10	35	5
2	50	10	50	5
3	100	60	165	

In Examples 33 to 48 Calcinate™ C300CS and Calcinate™ C400CLR are compared on the basis of equal weight..



TABLE 5

Example	31	32	33	34	35	36	37	38	39	40	41	42	43	44
C300CS	10%	10%	10%	10%	10%	10%	10%	-	-	-	-	-	-	-
C400CLR	-	-	-	-	-	-	-	10%	10%	10%	10%	10%	10%	10%
OCO	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-	-	-
Alox 165L	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-	-
OBT	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-
OCT	-	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-
GMO	-	-	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-
Tea-T	-	-	-	-	-	-	0.5%	-	-	-	-	-	-	0.5%
Dil Oil	89.5%	89.5%	89.5%	89.5%	89.5%	90%	89.5%	89.5%	89.5%	89.5%	89.5%	89.5%	90%	89.5%
CoF@60	0.1250	0.1125	0.1275	0.1125	0.1000	0.1267	0.1025	0.1325	0.1090	0.1060	0.1100	0.0960	0.1390	0.1210
70	0.1150	0.1050	0.1175	0.1060	0.0960	0.1258	0.0975	0.1375	0.1060	0.1125	0.1100	0.0910	0.1450	0.1265
80	0.1100	0.1025	0.1100	0.1020	0.0940	0.1222	0.0950	0.1390	0.1060	0.1150	0.1100	0.0900	0.1440	0.1270
90	0.0950	0.0950	0.1000	0.0975	0.0900	0.1160	0.0890	0.1375	0.1040	0.1060	0.1060	0.0875	0.1440	0.1270
100	0.0875	0.0860	0.0925	0.0910	0.0860	0.1115	0.0860	0.1375	0.1020	0.0980	0.1025	0.0850	0.1425	0.1265
110	0.0825	0.0825	0.0860	0.0890	0.0825	0.1013	0.0820	0.1375	0.1000	0.0910	0.1025	0.0840	0.1425	0.1245
120	0.0825	0.0790	0.0825	0.0850	0.0790	0.0945	0.0740	0.1325	0.0975	0.0840	0.1000	0.0810	0.1390	0.1213
130	0.0825	0.0775	0.0790	0.0810	0.0760	0.0908	0.0690	0.1300	0.0960	0.0760	0.0980	0.0800	0.1150	0.1163
140	0.0850	0.0760	0.0775	0.0800	0.0760	0.0883	0.0660	0.1325	0.0940	0.0760	0.0950	0.0790	0.1075	0.1150
150	0.0875	0.0800	0.0800	0.0790	0.0825	0.0867	0.0700	0.1340	0.0925	0.0660	0.0930	0.0775	0.1125	0.1125
160	0.0875	0.0800	0.0825	0.0800	0.0820	0.0858	0.0720	0.1275	0.0950	0.0590	0.0900	0.0750	0.1175	0.1090
Average	0.0945	0.0887	0.0941	0.0912	0.0858	0.1045	0.0821	0.1344	0.1002	0.0900	0.1015	0.0842	0.1317	0.1206

#### Examples 45-58

These Examples were conducted in a manner similar to those of Examples 33 to 49 except that Calcinat<sup>TM</sup> C300CS and Calcinat<sup>TM</sup> C400CLR were compared on the basis of equal TBN rather than equal weight. The results are set forth in Table 6.

TABLE 6

Example	45	46	47	48	49	50	51	52	53	54	55	56	57	58
C300CS	10%	10%	10%	10%	10%	10%	10%	-	-	-	-	-	-	-
C400CLR	-	-	-	-	-	-	-	10%	10%	10%	10%	10%	10%	10%
OCO	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-	-	-
Alox 165L	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-	-
OBT	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-	-
OCT	-	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-	-
GMO	-	-	-	-	0.5%	-	-	-	-	-	-	0.5%	-	-
TEA-T	-	-	-	-	-	-	0.5%	-	-	-	-	-	-	0.5%
Dil Oil	89.5%	89.5%	89.5%	89.5%	89.5%	90%	89.5%	89.5%	89.5%	89.5%	89.5%	89.5%	90%	89.5%
CoF@60	0.1250	0.1125	0.1275	0.1125	0.1000	0.1267	0.1025	0.1325	0.1090	0.1060	0.1100	0.0960	0.1390	0.1210
70	0.1150	0.1050	0.1175	0.1060	0.0960	0.1258	0.0975	0.1375	0.1060	0.1125	0.1100	0.0910	0.1450	0.1265
80	0.1100	0.1025	0.1100	0.1020	0.0940	0.1222	0.0950	0.1390	0.1060	0.1150	0.1100	0.0900	0.1440	0.1270
90	0.0950	0.0950	0.1000	0.0975	0.0900	0.1160	0.0890	0.1375	0.1040	0.1060	0.1060	0.0875	0.1440	0.1270
100	0.0875	0.0860	0.0925	0.0910	0.0860	0.1115	0.0860	0.1375	0.1020	0.0980	0.1025	0.0850	0.1425	0.1265
110	0.0825	0.0825	0.0860	0.0890	0.0825	0.1013	0.0820	0.1375	0.1000	0.0910	0.1025	0.0840	0.1425	0.1245
120	0.0825	0.0790	0.0825	0.0850	0.0790	0.0945	0.0740	0.1325	0.0975	0.0840	0.1000	0.0810	0.1390	0.1213
130	0.0825	0.0775	0.0790	0.0810	0.0760	0.0908	0.0690	0.1300	0.0960	0.0760	0.0980	0.0800	0.1150	0.1163
140	0.0850	0.0760	0.0775	0.0800	0.0760	0.0883	0.0660	0.1325	0.0940	0.0760	0.0950	0.0790	0.1075	0.1150
150	0.0875	0.0800	0.0800	0.0790	0.0825	0.0867	0.0700	0.1340	0.0925	0.0660	0.0930	0.0775	0.1125	0.1125
160	0.0875	0.0800	0.0825	0.0800	0.0820	0.0858	0.0720	0.1275	0.0950	0.0590	0.0900	0.0750	0.1175	0.1090
Average	0.0945	0.0887	0.0941	0.0912	0.0858	0.1045	0.0821	0.1344	0.1002	0.0900	0.1015	0.0842	0.1317	0.1206

### Examples 59-74

A study was made of various friction modifiers to determine sedimentation at 12 weeks . The Experiments were conducted by blending crystalline overbased calcium sulfonate Calcinat C300CS ( 10 wt%) with Hyprene H100 lubricant oil stock, and 0.5 % of the selected friction modifier. The composition was then placed in a 70°C oven in a 100 ml centrifuge tube and the sediment formed was measured at one week intervals. The sediments formed ranged from flocculant white/gray material to black solids, although no attempts were made to separately quantify the different types observed. Rather, only the total amount of sediment observed in the centrifuge was recorded so that simple comparisons could be made. The total amount of sediments formed at the end of the 12 week period are reported in Table 7. For comparison, the blend of Calcinat C300CS plus lubricant oil but without a friction modifier was conducted to provide a baseline comparison and was recorded at 0.25%. The mixed oleic/stearic glycol is available from Arizona Chemical Co. under the designation Uniflex 1803. The friction modifiers of Examples 65-74 are the reaction products of the specified compounds.

As can be seen the use of friction modifiers comprising the reaction product of TEA with methyl oleate, tall oil fatty acid, oleic acid, isostearic acid and mixed oleic/stearic acids resulted in low sedimentation as compared with the baseline level of 0.25%. Also, the use of the reaction product of thiodiglycol and methyl oleate resulted in low sedimentation. Overbased alkaline earth carboxylates also provided low sedimentation.

Table 7

Example	Friction Modifier	Sediment (12 Weeks)
59	Glycerol mono oleate	0.25%
60	Overbased calcium carboxylate (OCO)	0.25%
61	Overbased barium carboxylate (OBT)	0.05%
62	Overbased calcium carboxylate (OCT)	0.15%
63	Oxidized petrolatum (Alox 165L)	0.30%
64	Mixed oleic/stearic glycol (Uniflex 1803)	0.25%
65	TEA + methyl oleate	0.05%
66	TEA + tall oil fatty acid	0.06%
67	TEA + oleic acid	0.05%
68	TEA + ricinoleic acid	5.10%
69	TEA + isostearic acid	0.15%
70	TEA + erucic acid	0.35%
71	TEA + mixed oleic/stearic acids	0.20%
72	TEA + iso-oleic acid	1.10%
73	Thiodiglycol + methyl oleate	0.20%
74	Diethylene glycol + methyl oleate	4.20%

Example 75

The sedimentation tests of Examples 59 to 74 were extended past the 12 week period to determine the nature of failure mode of separation. The results of selected friction modifiers are shown in FIG. 1. A comparison is made with friction modifier produced by the reaction of TEA with a monomeric fatty acid distillate obtained from the dimerization of tall oil fatty acid, such as a mixture of branched and straight chain fatty acids available from Arizona Chemical Co. under the designation Century™ D-1. Also shown in FIG. 1 are the sedimentation test results of a friction modifier produced by the

reaction of TEA with a mixture of C18 mon-unsaturated mostly methyl branched fatty acids, available from Arizona Chemical Co. under the designation Century™ D1164.

The results show an initial induction period of very low sedimentation followed by a catastrophic failure the sediment completely precipitates in a one week period forming a distinct layer. The layer then continues to compact over the next 2 - 4 weeks and reduces the sediment volume, as can be seen from the TEA + ricinoleic acid, or diethylene glycol + methyl oleate tests. In a second mode the sediment layer forms more slowly after the induction period, but a flocculant material is observed in the supernatant liquid. While the sediment layer does not settle any further, the floc in the supernatant liquid appears to separate into a distinct layer which causes the level of sediment to increase over time, as can be seen from the tests involving TEA + TOFA, TEA + oleic acid, and TEA + iso-oleic acid. There does not appear to be any correlation between the failure mode and the structure of the friction modifier used. However, while not wishing to be bound to any specific theory, it is suggested that the formation of a more dense sediment would more completely separate in the catastrophic failure mode whereas a lighter precipitate would tend to flocculate and settle more slowly after failure.

#### Example 76

Friction tests were performed on selected combinations of overbased calcium sulfonate and friction modifiers of Example 75 in accordance with the testing method set forth in Examples 31-58. The results are illustrated in FIG.2.

It can readily be appreciated that storage of a lubricant oil composition in a vessel over an extended period of time can be accompanied by much less sedimentation by adding to a lubricant stock a mixture including an overbased alkaline earth metal sulfonate, such as overbased calcium sulfonate, and a friction modifier in accordance with the invention.

#### Example 77

This Example illustrates the preparation of the reaction product of TEA with tall oil fatty acid.

A 250mL 3-neck round-bottom flask equipped with an agitator, thermocouple and distillation condenser was charged with 0.062 mol triethanol amine, 0.185 tall oil fatty acid and 0.003 mol para-toluene sulfonic acid catalyst. The system was purged with nitrogen for 3-4 minutes, then the nitrogen flow was turned down to a minimum. The system was agitated and heated to 160°C. Once at this temperature, the nitrogen flow was increased to facilitate the removal of water. Conditions were held for 5 hours after which time IR analysis showed the acid carbonyl absorbance (1712 cm<sup>-1</sup>) to be absent. The reaction was cooled to 100°C and the catalyst was neutralized with 0.70 grams of a Hitec 611 (a 300 TBN detergent). The reaction was filtered to remove solids. The product obtained, was 62 grams of light amber, low viscosity liquid.

### Example 78

This example illustrates the synthesis of a reaction product of diethylene glycol with methyl oleate to obtain ethylene glycol dioleate.

25 Parts of diethylene glycol and 139.7 parts of methyl oleate were combined in a 3-neck round bottom flask. The mixture was heated to 100°C with stirring under a nitrogen sweep. At 100°C, 0.26 parts of dibutyl tin diacetate catalyst was added and the mixture was then heated to 180°C. After 4.33 hours the system was cooled to 100°C and 1.1 parts of Filtrol 20x acid clay was added to neutralize the catalyst. The system was stirred for 15 minutes and the contents of the flask were then filtered with vacuum. The final product was 136.43 parts of low viscosity dark yellow fluid.

While the above description contains many specifics, these specifics should not be construed as limitations of the invention, but merely as exemplifications of preferred embodiments thereof. Those skilled in the art will envision many other embodiments within the scope and spirit of the invention as defined by the claims appended hereto.